



Controls on anthropogenic radionuclide distribution in the Sellafield-impacted Eastern Irish Sea

Daisy Ray^{a,1}, Peter Leary^b, Francis Livens^{a,c}, Neil Gray^b, Katherine Morris^c, Kathleen A. Law^{a,d}, Adam J. Fuller^{a,2}, Liam Abrahamsen-Mills^e, John Howe^f, Kieran Tierney^{g,3}, Graham Muir^g, Gareth T.W. Law^{a,d,*}

^a Centre for Radiochemistry Research, Department of Chemistry, School of Natural Sciences, The University of Manchester, Manchester M13 9PL, UK

^b School of Natural and Environmental Sciences, Newcastle University, Newcastle NE1 7RU, UK

^c Research Centre for Radwaste and Decommissioning and Williamson Research Centre, Department of Earth and Environmental Sciences, School of Natural Sciences, The University of Manchester, Manchester M13 9PL, UK

^d Radiochemistry Unit, Department of Chemistry, The University of Helsinki, Helsinki 00014, Finland

^e National Nuclear Laboratory, Chadwick House, Birchwood, Warrington WA3 6AE, UK

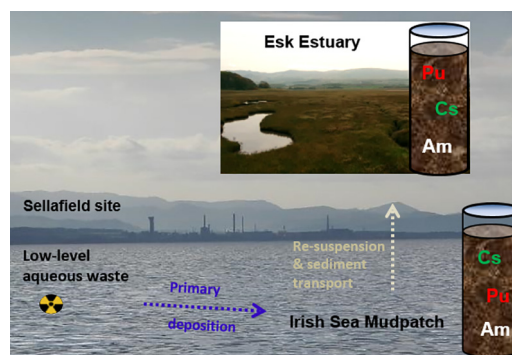
^f Scottish Association for Marine Science, Scottish Marine Institute, Dunbeg-by-Oban PA37 1QA, UK

^g Scottish Universities Environmental Research Centre, Scottish Enterprise Technology Park, Rankine Avenue, Glasgow G75 0QF, UK

HIGHLIGHTS

- Discharge of low-level waste from the Sellafield site into the Irish Sea for >50 y.
- ¹³⁷Cs, Pu, and ²⁴¹Am have accumulated in the Irish Sea Mudpatch.
- Physical redistribution of sediment largely controls contaminant distribution.
- Sediment biogeochemistry does not significantly influence Pu distribution.
- Mudpatch acts as a buffer and source of historical anthropogenic radioactivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding anthropogenic radionuclide biogeochemistry and mobility in natural systems is key to improving the management of radioactively contaminated environments and radioactive wastes. Here, we describe the contemporary depth distribution and phase partitioning of ¹³⁷Cs, Pu, and ²⁴¹Am in two sediment cores taken from the Irish Sea (Site 1: the Irish Sea Mudpatch; Site 2: the Esk Estuary). Both sites are located ~10 km from the Sellafield nuclear site. Low-level aqueous radioactive waste has been discharged from the Sellafield site into the Irish Sea for >50 y. We compare the depth distribution of the radionuclides at each site to trends in sediment and porewater redox chemistry, using trace element abundance, microbial ecology, and sequential extractions, to better understand the relative importance of sediment biogeochemistry vs. physical controls on radionuclide distribution/post-depositional mobility in the sediments. We highlight that the distribution of ¹³⁷Cs, Pu, and ²⁴¹Am at both sites is largely controlled by physical mixing of the sediments, physical transport processes, and

* Corresponding author at: Centre for Radiochemistry Research, Department of Chemistry, School of Natural Sciences, The University of Manchester, Manchester M13 9PL, UK.

E-mail address: gareth.law@helsinki.fi (G.T.W. Law).

¹Current address: UK Department for Business, Energy and Industrial Strategy, 1 Victoria Street, London, SW1H 0ET, UK.

²Current address: Galson Sciences Ltd., 5 Grosvenor House, Melton Road, Oakham, Rutland, LE15 6AX, UK.

³Current address: Department of Civil and Environmental Engineering, University of Strathclyde Glasgow, Montrose Street, Glasgow, G1 1XJ, UK.

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sediment accumulation. Interestingly, at the Esk Estuary, microbially-mediated redox processes (considered for Pu) do not appear to offer significant controls on Pu distribution, even over decadal timescales. We also highlight that the Irish Sea Mudpatch likely still acts as a source of historical pollution to other areas in the Irish Sea, despite ever decreasing levels of waste output from the Sellafield site.

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1. Introduction

The authorised discharge of low-level aqueous radioactive waste from the Sellafield nuclear site (Cumbria, UK) to the Eastern Irish Sea has taken place since 1952 (Kershaw et al., 1992; Gray et al., 1995). Liquors from spent fuel reprocessing and purge waters from fuel storage ponds are the major contributors to this waste stream, and they contain a range of actinides and fission products (e.g. Cs, U, Np, Pu, and Am) (Kershaw et al., 1992). Since 1952, the discharges have varied due to changing practices on-site (Kershaw et al., 1992; Gray et al., 1995). Discharge activities increased throughout the 1960s due to elevated waste throughput and processing. They then peaked in the mid-1970s due to increased storage times for Magnox fuels (Kershaw et al., 1992). Thereafter, discharge activities decreased significantly as new effluent treatment technologies were commissioned (Kershaw et al., 1992). Current discharges are now three orders of magnitude lower than historical maxima, and are well below authorised limits (Sellafield Ltd., 2017). As the site is now transitioning from spent fuel reprocessing to decommissioning and post operational clean-out, the discharges should continue to decrease.

The Sellafield discharges are neutralised to pH ~7 on-site prior to disposal into the Eastern Irish Sea, via a pipeline extending 2.1 km seaward from the low water mark (Kershaw et al., 1992). Once disposed, the chemistry of the radionuclides and that of the local environment (e.g. Eh, pH, salinity, availability of complexants, sorption sites etc.) determine whether the discharged activity concentrates in local coastal areas. In this paper we focus on the environmental behaviour of Sellafield-derived ^{137}Cs , Pu, and ^{241}Am .

Cesium is present as the Cs^+ cation in seawater, with a measured K_d of 10^3 – 10^4 (Hunt and Kershaw, 1990). Cesium can become associated with sediments via cation exchange, sorption to mineral surfaces, or incorporation into the interlayer of clay minerals (e.g. Cornell, 1992; Chibowski and Zygmunt, 2002; Fuller et al., 2015). A sizeable fraction of Sellafield-derived ^{137}Cs (~10%) is thought to have been removed from local seawater via reaction with clay minerals (Jones et al., 1999). Plutonium can co-exist in up to four oxidation states (III–VI) under normal environmental conditions (Morse and Choppin, 1991). In marine systems, particle reactive Pu(III) and more soluble Pu(V) are the dominant species, although Pu(III) and Pu(IV) can also exist, giving Pu a broad K_d (10^4 – 10^6) (McDonald et al., 2001). Plutonium (III/IV) species readily undergo hydrolysis, and in marine systems are thought to be scavenged by suspended particles (Nelson and Lovett, 1978). A wide range of studies have shown Pu reactivity towards a range of mineral surfaces (e.g. Fe and Mn oxy(hydr)oxides, clays, and quartz) (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Lu et al., 2003; Lujanienė et al., 2007; Begg et al., 2013). Surface mediated reduction of Pu(V) to less mobile Pu(IV) on minerals, as well as microbial reduction of Pu(V), has also been observed (e.g. Powell et al., 2005; Icopini et al., 2009; Renshaw et al., 2009; Zavarin et al., 2012). It has been suggested that >90% of the Pu discharged into the Irish Sea has become associated with sediments as Pu(IV) (MacKenzie and Scott, 1993). The remaining 10% is thought to form Pu(V/VI) dioxocations (e.g. PuO_2^+ and PuO_2^{2+}) that remain in the seawater (MacKenzie et al., 1999). Finally, ^{241}Am is commonly found in the environment as poorly soluble ($K_d = 10^6$) Am(III) (McDonald, 2011). The high charge density of Am(III) means that it readily undergoes hydrolysis, forming precipitates and/or sorbing to geomedial. As a consequence,

Am is generally thought to be associated with colloids, sediment, and humic materials (MacKenzie et al., 1994). The majority of Sellafield derived ^{241}Am is suggested to have become associated with fine-grained sediments (MacKenzie et al., 1999).

Interestingly, a large proportion of the Sellafield-derived radionuclides disposed to sea have become associated with the sediment at two sites close to the waste disposal pipeline: (1) the Irish Sea Mudpatch (herein, Mudpatch), and (2) the Esk Estuary. The Mudpatch is a belt of fine-grained sediments located ~10 km from the waste pipeline. It is thought that a fraction of the disposed radionuclides associate with fine-grained sediments suspended in the water column. Some of this material is then deposited at the Mudpatch, and thereafter indigenous macrobenthic organisms mix the radionuclides through the sediment profile to depths of ~1–1.5 m. MacKenzie et al. (1998) determined that the Mudpatch sediments record an integrated (as opposed to time-resolved) inventory of the Sellafield low level waste discharges due to this mixing. The action of the microbenthic organisms, combined with bottom water currents, mean that some of the deposited radionuclides can be remobilised into the water column. This can occur via redissolution of the radionuclides into the overlying water, or resuspension of radiolabelled sediment (Kershaw et al., 1983; Kershaw et al., 1984; McCartney et al., 1994; Kershaw et al., 1999). Sequential extraction studies completed with Mudpatch sediments suggest that ^{137}Cs , Pu, and ^{241}Am are (largely) chemically unavailable and as such, resuspension and physical transport have been suggested to dominate radionuclide transport from the Mudpatch (MacKenzie et al., 1987; MacKenzie and Scott, 1993). MacKenzie et al. (1998) have however documented substantial Cs release from Mudpatch surface sediments, and the more recent work of Gouzy et al. (2005) suggests that Pu may be more chemically available than previously thought. Here, anoxic conditions at depth on the Mudpatch are suggested to partition Pu onto the solid phase (e.g. via reaction with acid volatile sulphide (AVS) phases). Plutonium could then be re-released into the water column due to bioturbation and oxidative dissolution of Pu bearing phases.

Regardless, once mobilised, the radionuclides can be transported elsewhere in the Irish Sea by currents and historically, this has been used to explain widespread radionuclide contamination of UK and Irish marine sediments (e.g. Aston and Stanners, 1981a, 1981b; McCartney et al., 1994; Morris et al., 2000; Keogh et al., 2007). Although waste discharges are continuing to decrease from the Sellafield site, the Mudpatch may continue to supply “historic” Sellafield-derived radionuclides to other locations. Indeed, recent data from Welsh and Scottish coastal areas (Al-Qasbi et al., 2016, 2018) suggest that the Mudpatch still acts as a source of radionuclides to UK coastal areas. However, the most recent data from the Mudpatch stems from a survey conducted in 2002 (Gouzy et al., 2005). Re-evaluating the distribution, biogeochemistry, and sediment partitioning of ^{137}Cs , Pu, and ^{241}Am at this site is important if we are to better understand longer-term trends.

In contrast, the Esk Estuary is a low-energy intertidal region ~10 km to the south of Sellafield. Radionuclide distribution and biogeochemistry at the site has been extensively studied (e.g. Aston and Stanners, 1981a, 1981b; Morris et al., 2000; Lucey et al., 2004; Marsden et al., 2006; Lindahl et al., 2011; Oh et al., 2009; Sajih and Livens, 2010; Caborn et al., 2016). The re-suspension of Mudpatch sediment followed by transport to, and deposition at the estuary, has been invoked as a key mechanism controlling radionuclide deposition in this area (Aston et al., 1985; Kershaw et al., 1990; McCartney et al., 1994; Morris et al., 2000;

Marsden et al., 2006). Because sediment mixing at the Esk Estuary is limited, radionuclide depth distribution at the site preserves the Sellafield discharge signal. However, some degree of post-depositional remobilisation has been noted (e.g. due to tidal induced changes in porewater redox chemistry, mineral dissolution etc.; Morris et al., 2000; Marsden et al., 2006; Finegan et al., 2009). Sequential extractions performed on Esk estuary sediments have shown significant variability in radionuclide partitioning (e.g. Mudge et al., 1988; Lucey et al., 2004; Kimber et al., 2015), and some studies have shown that radionuclides can be lost from the sediment to the site's overlying waters (e.g. MacKenzie et al., 1987; Hunt and Kershaw, 1990; McDonald et al., 1998; Keith-Roach et al., 2000). Continued monitoring of radionuclide distribution and behaviour in the publicly accessible Esk Estuary sediments is clearly required.

Reflecting on the above, here we report on the distribution of Sellafield-derived ^{137}Cs , Pu, and ^{241}Am in sediment cores sampled from the Mudpatch and Esk Estuary in 2014. Our objective was to determine the contemporary factors controlling radionuclide retention/availability at both sites. We relate the measured radionuclide distribution profiles to historical Sellafield discharge records and sediment/porewater stable element geochemistry. To provide a more integrated view of each site's biogeochemistry, for the first time we also document and describe each site's microbial ecology. Finally, we use sequential extractions to better define the geochemical association of ^{137}Cs , Pu, ^{241}Am in the sediments. Combined, these results provide a unique insight into long-term anthropogenic radionuclide behaviour in coastal environments; although we stress that due to inherent heterogeneity at our study sites, direct comparisons between previously reported activities in these locations are limited; however, comparisons of activity profiles and general trends can be made.

2. Methods and materials

2.1. Sample collection and preparation

Sediment cores were collected from a belt of fine-grained sediment in the north-east Irish Sea Mudpatch, (54°26.80 N, 03°42.89 W) in June 2014 and from the Esk Estuary (54°20.24 N, 03°24.06 W, respectively) in September 2014 (see Fig. S1 for a map of the study sites). Sediment cores (depth ~35 cm, diameter 10 cm) were retrieved from the Mudpatch using a hydraulic mega-corer (Law et al., 2009). Care was taken during coring to leave the sediment–water interface as undisturbed as possible. Cores from the Esk Estuary (depth ~30 cm, diameter 10 cm) were collected by manual insertion of core tubes, with an air-tight bung placed over the top and bottom of the core during extraction. Two cores from each of the study sites were used for analyses. One core from each site was sectioned within 1 h of collection under a O_2 free N_2 atmosphere. The second was sampled under a normal atmosphere ~6 h after collection. The cores were sectioned at 1 cm resolution from the sediment interface to a depth of 10 cm, and at 2 cm thereafter. Porewater from each section in the first core was collected by centrifugation (10 min at 4500 rpm; 1811g) followed by filtration (0.22 μm PTFE membrane syringe filters). The filtered solutions were then fixed via addition of 200 μL Aristar grade concentrated HNO_3 .

2.2. Total organic matter

Sequential Loss on Ignition (LOI) was used to determine the total organic matter present in the sediment samples. Here, homogenised sediment (~5.5 g) from each sample was oven dried at 105 °C for 24 h, then heated at 375 °C for 19 h using a ramp rate of 1 °C/min, and finally ashed at 950 °C for 10 h using a ramp rate of 10 °C/min. These heating stages were used to eliminate water and organic matter (Rowell, 1994).

2.3. Elemental analysis of sediment and porewater

The concentration of Al, Fe, K, Mg, Mn, and P in the bulk sediment was measured using a Panalytical Axios sequential XRF. Ground sediment (12 g) was added to powdered wax binder (3 g) and homogenised (7 min at 350 rpm) in an agate ball mill, and then pressed into pellets under pressure (7–10 t). The pellets were analysed, and the resulting data were oxide normalised and corrected for C content.

Acidified porewater (200 μL) samples were diluted in 2% HNO_3 (4.8 mL) and analysed for Fe and Mn on a Perkin Elmer Optima 5300 Dual View ICP-AES.

2.4. Microbial community analysis

DNA was extracted from sectioned core samples using a FastDNA Spin Kit for Soil (MP Biomedicals) as per the manufacturer's instructions. DNA underwent PCR, using the universal primer pair F515 and R926 (positions 515 to 926 in the V4–V5 region of the 16S rRNA gene; *Escherichia coli* numbering), which target both bacteria and archaea. Forward primers used 'goyal_12' barcodes and Torrent adaptor A for identification. Initial denaturation was at 95 °C for 5 min; 30 cycles of 95 °C for 1 min, 55 °C for 1 min, 72 °C for 1 min; and a final elongation step of 72 °C for 10 min. PCRs were performed on a Techne 512 thermocycler, and in triplicate to reduce bias. Amplicons were cleaned using Agencourt AMPure XP (Beckman Coulter), quantified via Qubit 3.0 fluorometer (Life Technologies) and pooled.

Sequencing was performed on an Ion Torrent Personal Genome Machine (Thermo Fisher Scientific) on a 316 chip. Sequencing produced reads with a modal length of 481 bases. The average number of reads in individual binned closed-reference core section libraries after filtering and operational taxonomic unit (OTU) phylogenetic assignment filtering was 14,836.41 for the Mudpatch, ranging from 5808 to 23,402. The average number of reads was 13,271.68 for the Esk Estuary, ranging from 6922 to 21,972. Libraries were rarefied to 5800 sequences for the Mudpatch core, and 6900 sequences for the Esk Estuary core to allow for comparative analysis of sequences between different core sections. Sequences for both sediment cores were deposited in the NCBI's Sequence Read Archive (SRA), and are available under BioProject PRJNA625461. Pipeline analysis was performed using QIIME 1.9.1, (2010) with OTU matching performed at 99% similarity against the SILVA128 closed-reference database (2012). OTU tables were standardised by total for each sample depth, and square root transformed, in PRIMER 6 (Clarke and Gorley, 2005). Bray Curtis similarity and non-metric-Multidimensional Scaling analysis was then performed. Taxonomy summary bar charts are used to represent trends in community change as a function of depth (based on assignments of OTUs to the genus level where possible). Dominant taxa and their abundance change with depth were related to other geochemical parameters based on geochemical functions inferred from the conserved phenotypic characteristics of close relatives.

2.5. Measurement of ^{137}Cs and ^{241}Am

The activity of ^{241}Am and ^{137}Cs in sediment pellets were measured by gamma counting (24 h) on a lead shielded Canberra GC1019 hyper-pure germanium (HPGe) detector. The detector was calibrated for efficiency using matrix and geometry matched standards that were spiked with certified standard solutions of ^{241}Am and ^{137}Cs (Amersham International). Gamma spectra were also corrected for background. All activities were decay corrected to the date of sample collection.

2.6. Measurement of ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Pu

^{238}Pu , and $^{239,240}\text{Pu}$ alpha activity was measured using a Canberra 7401 α -spectrometer and ^{241}Pu activity was measured using a 1220 Quantulus ultra low level liquid scintillation spectrometer. Pu

separation was based on that of Nygren et al. (2003) using Eichrom TEVA® resin and full details of the method are provided in the SI (section S1). All activities were decay corrected to the date of sample collection.

2.7. Sequential extraction

The partitioning of ^{137}Cs , $^{239,240}\text{Pu}$, and ^{241}Am in the sediments from the Mudpatch and Esk Estuary was investigated for select samples using a modified Tessier extraction (Tessier et al., 1979; Keith-Roach et al., 2003; Begg et al., 2011). ^{137}Cs and ^{241}Am extractions were performed on 10 core sections due to the ease of later measurements; $^{239,240}\text{Pu}$ extractions were performed on 2 core samples due to the more complicated nature of Pu measurement. The extraction procedure is summarised in Table 1 and further details are provided in the SI (section S2).

3. Results and discussion

3.1. Sediment biogeochemistry and major element distribution

The total organic matter content of the Mudpatch was relatively constant with depth at ~1 wt% (Table S1), suggesting that organic matter input and turnover at this site is low. In the Esk Estuary, the total organic matter content ranged from ~7 wt% at the sediment surface to ~4 wt% at depth (Table S2), possibly reflecting microbially-mediated oxidation of organic matter (Froelich et al., 1979). Sediment grain size measurements were not attempted in this study but in the past the Mudpatch sediments have been shown to be comprised of fine sand (46%), silt (37%), and clay (13%) (McDonald et al., 1990). Sediment in the Esk Estuary has been shown to be predominantly comprised of silt (~75%), clay (~19%), and sand (7%) (Morris et al., 2000). At both sites, the concentration of the lithogenic elements (Al, Mg, K) varied little with depth (Table S1 and S2, respectively). The concentration of P at the Mudpatch ranged between 0.04 and 0.1 wt%, with no trend (Table S1). In some marine sediment systems, higher P concentrations are observed in surface sediments reflecting an input of labile organic matter. The low concentration of P and total organic matter observed at this site during sampling (which took place during the British Summer, when marine productivity is at its highest) indicates that this sediment system likely remains organic-poor year-round. Marginally higher P concentrations were found in the Esk Estuary sediments (0.12–0.16 wt%; Table S2) but there was little variation with depth.

Porewater analysis for NO_3^- was attempted at both sites but analyte concentrations were below the limit of detection (0.05 mg/L) for all samples. Fig. 1A and C show the distribution of solid phase Mn (expressed as a Mn/Al ratio to remove variance from the detrital (non-reactive) fraction; Calvert and Pedersen, 1993) in the Mudpatch and Esk Estuary cores, respectively. There was an enrichment of Mn close to the surface at both sites, however this was more marked at the Mudpatch. The Mn enrichment is probably due to the input of Mn-oxy(hydr)oxides as grain coatings (Calvert and Pedersen, 1993). At the Mudpatch, the Mn/Al ratio decreased from the surface to 5 cm depth, which is consistent with microbially-mediated reduction of Mn-oxy(hydr)oxides (Froelich et al., 1979). In turn, Mn porewater concentrations at the Mudpatch were enhanced (248–345 μM) between 0 and 4 cm (Fig. 1E). They then decreased to 17 μM at 35 cm, likely reflecting gradual Mn sorption to the sediment. At the Esk Estuary, the Mn/Al ratio decreased between 0 and 5 cm (Fig. 1C) commensurate with a subsurface peak in porewater Mn (Fig. 1G), with Mn concentrations reaching a maximum (104 μM) at 1 cm and decreasing to 4.1 μM by 6 cm. This porewater subsurface maximum and decrease in the Mn/Al ratio between 0 and 6 cm suggests that some microbially-mediated Mn(IV) reduction does occur at this site. However, whilst the porewater Mn concentrations at the Esk Estuary remained below 5.0 μM after a depth of 6 cm, the Mn/Al ratio did show a sub-surface

maxima between 14 and 22 cm. The origin of this maximum is unclear but it should be noted that during rising tides, water can pump upwards through channels in the sediment. This undoubtedly complicates the development of depth-related changes in redox processes at this site.

The sediment Fe/Al ratios at the Mudpatch and Esk Estuary sites (Fig. 1B and D) showed a similar trend with higher, near-constant ratios in the upper sections (0–12 cm) of each core. There was then a steady decrease in the Fe/Al ratio to 18 cm depth at the Mudpatch, and 24 cm at the Esk Estuary, likely reflecting microbially-mediated reduction of Fe(III) (Froelich et al., 1979). The Fe/Al ratios then increased slightly towards the bottom of the cores. Porewater Fe concentrations at the Mudpatch were variable between 0 and 5 cm (Fig. 1F), showing a subsurface peak (226 μM) at 2 cm and near-zero concentrations at the sediment surface and between 3 and 5 cm. Below 5 cm, the porewater Fe concentrations then increased to 166 μM at 6.5 cm and gradually decreased to 39 μM by 35 cm, likely reflecting Fe(II) sorption to the deeper sediments or possibly precipitation of authigenic Fe(II) bearing phases (Calvert and Pedersen, 1993). At the Esk Estuary, porewater Fe concentrations were similar to the Mudpatch, highlighting a variable trend between 0 and 5 cm, with a subsurface peak (152 μM) at 2.5 cm, and low Fe concentrations (18 μM) at 1 cm (Fig. 1H). Thereafter, there was an increase to 100 μM at 6.5 cm, followed by a gradual decrease in concentration, likely for similar reasons as suggested for the Mudpatch. Overall, the trends in sediment and porewater Fe likely reflect the input of Fe(III)-oxy(hydr)oxides to the surface sediments of both sites followed by microbially mediated Fe bio-cycling (Burdige, 1993), overlain by the complicating impacts of bioturbation (Mudpatch) and tidal effects (Esk Estuary).

3.2. Characterisation of the microbial community

Typically, in a vertical soil or sediment profile, a thermodynamically controlled respiratory redox stratification of microbial metabolism can be observed, which proceeds from aerobic through to anaerobic and fermentative processes (Froelich et al., 1979). Whilst the distribution of Mn and Fe in the sediments and porewaters of both sites indicated a transition to more suboxic conditions with depth, we aimed to better assess (over a longer time period) the dominant redox processes at the Mudpatch and Esk Estuary sites by quantifying the presence and distribution of certain functionally indicative microbial taxa. This assessment was based on an assumed turnover of DNA within a sediment of <2 years (Nielsen et al., 2006) and whether incrementally progressive successional patterns as a function of core depth could be observed. The identification of such key functional microbial taxa via DNA has the potential to provide a time averaged picture of the dominant sediment biogeochemistry.

We found that the microbial community assemblages of both the Mudpatch and Esk Estuary sediment systems did not conform to a simple vertical diffusional controlled respiratory succession, however, the distribution patterns observed were distinctive and informative of the prevailing geochemical and physical conditions at each location. The microbial community at the Mudpatch was reasonably homogeneous with depth (Fig. 2A). However, there were several discrete horizons characterised by the dominance of specific microbial taxa. At a depth of 0–1 cm the aerobes *Psychrobacter* spp. (41% of library sequences) and *Lutimonas* spp. (22%) dominated (Fig. 2D and C) (Caporaso et al., 2010; Romanenko et al., 2009; Teixeira and Merquior, 2014). Then, between 3 and 5 cm, 16–18 cm, and 20–22 cm the aerobic/facultative anaerobic family *Planococcaceae* (Fig. S2) dominated, ranging from 49 to 69% of sequences (Figs. 2F and S3) (Shivaji et al., 2014), with the presence of the *Planococcaceae* genera, *Jeotgalibacillus* sp. (21%) (Figs. S2 and S3) found in the deeper region of the core. These instances of community dominance at discrete horizons may be indicative of physical mixing by indigenous macrofauna. Past work close to our Mudpatch sampling site refers to the presence of a large echinuran (*Maxmulleria lankesteri*) known to burrow to a depth of ~1.5 m (Kershaw et al.,

Table 1

Summary of the extraction procedure used to investigate radionuclide, Fe, and Mn partitioning in select sediment samples.

Fraction name	Reagent	Time and temperature	Targeted phase(s)
Exchangeable	MgCl ₂ (1 M, pH 7)	2 h at room temperature	Exchangeable/readily available
Reducible	(NH ₄) ₂ C ₂ O ₄ (0.1 M) adjusted to pH 2–3 with 0.1 M HCl	17 h at room temperature	Reducible oxide bound
Oxidisable	H ₂ O ₂ (30%) adjusted to pH 2–3 with HNO ₃ , heated to complete dryness, then leached with ammonium acetate (0.1 M) in 6% (v/v) HNO ₃ (pH 2)	24 h at 80 °C then 6 h at room temperature	Sulfides/organic matter bound
Residual	<i>Aqua regia</i> (3:2 v/v HCl: HNO ₃)	3 h at ~80–110 °C	Aluminosilicates/refractory minerals

1984). The remainder of the Mudpatch samples shared a similar, highly diverse, microbial community assemblage, showing a mix of strict aerobes, and facultative and strict anaerobes (Fig. 2A). Aerobic taxa include the family *Planctomycetaceae* ($6.3 \pm 0.6\%$) (Fig. S3), and the ammonia oxidising phylum *Thaumarchaeota* ($1.3 \pm 0.2\%$) (Fig. S3) (Swan et al., 2014). Anaerobic taxa include the sulfate-reducing genus *Desulfobulbus* ($4.9 \pm 0.4\%$) (Figs. 2B and S2) (Kuever, 2014a), and the syntrophic/sulfate reducing family *Syntrophobacteraceae* ($2.9 \pm 1.5\%$) (Fig. S3) (Kuever, 2014b). This heterogeneity in respiratory function and homogeneity in the microbial community structure is potentially indicative of relatively low levels of microbial activity, likely consistent with physical mixing and the limited supply of organic matter at the Mudpatch site.

In contrast, the microbial community within the Esk Estuary sediment core showed marked transitions in community assemblage, most clearly demonstrated by the separation of two halves of the core based on depth (via Bray-Curtis analysis of community variation) at the ~7–8 cm horizon (Fig. 3A). However, even within these two

separated groups there was internally a clear successional depth related change in community composition (Fig. 3A). Similar to the Mudpatch, the 0–4 cm zone contained both aerobic and anaerobic taxa. *Bacterioidetes* families, including *Flavobacteriaceae* ($11.8 \pm 2.9\%$) and *Draconibacteriaceae* ($3.3 \pm 0.8\%$) (Figs. 3F and S4) (McBride, 2014; McIlroy and Nielsen, 2014), and also the anaerobic families *Anaerolineaceae* ($3.4 \pm 0.5\%$) and anaerobic sulfate-reducing *Desulfobulbaceae* ($6.1 \pm 0.7\%$) (Fig. S4) (Yamada et al., 2006; Kuever, 2014a; Thauer et al., 1977) were observed here. The 5–16 cm depth succession then encapsulates the major transition in microbial community structure as measured by Bray-Curtis nMDS (Fig. 3A). *Flavobacteriaceae* and *Desulfobulbaceae* amongst others, declined in abundance coincident with the emergence of the sulfate-reducing *Desulfobacteraceae* ($4 \pm 0.6\%$) (Fig. S4) (Kuever, 2014a), and the micro-aerobic, nitrogen-fixing *Rhodospirillaceae* ($4.4 \pm 0.3\%$) (Baldani et al., 2014). The ammonia oxidising *Thaumarchaeota* ($1.7 \pm 0.2\%$) (Figs. 3C and S4) (Swan et al., 2014) and the methane cycling *Bathyarchaeota* ($1.1 \pm 0.1\%$) (Figs. 3D and S4) (Evans et al., 2015) further highlight the complex assemblage

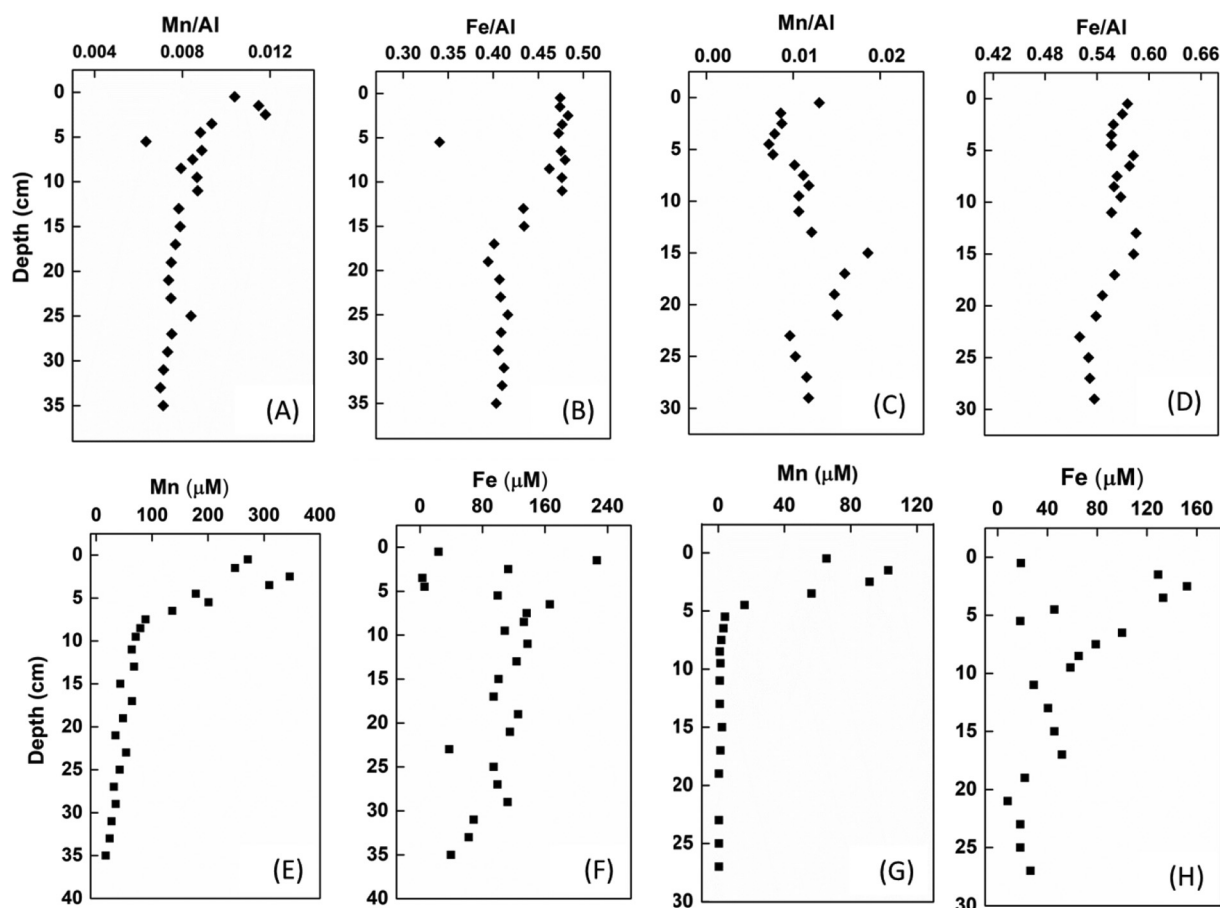


Fig. 1. Sediment Mn/Al and Fe/Al ratios in the Irish Sea Mudpatch (A and B) and Esk Estuary (C and D) and porewater Fe and Mn concentrations in the Irish Sea Mudpatch (E and F) and Esk Estuary (G and H). Note each x-axis is different so as to best highlight trends in the data.

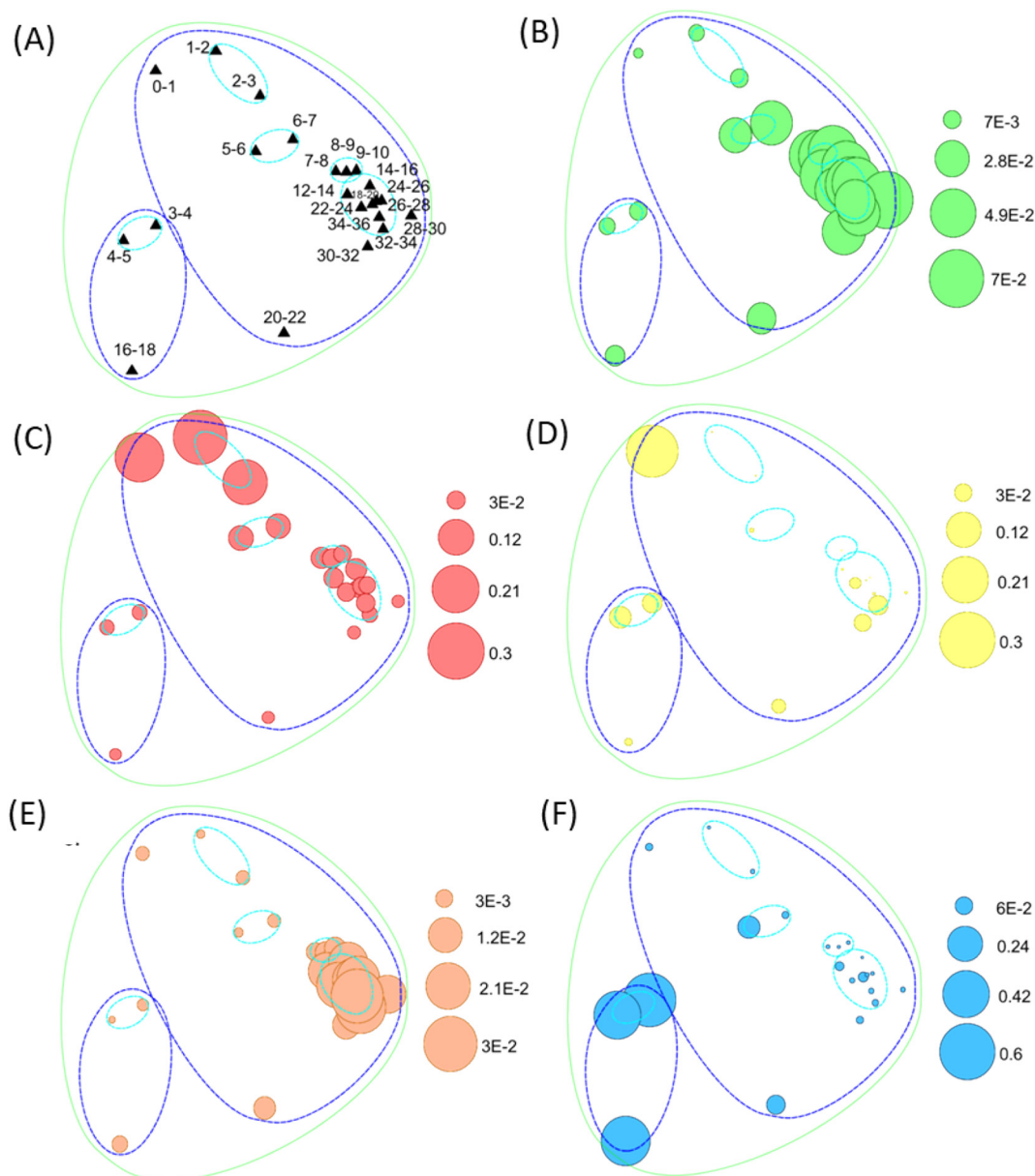


Fig. 2. For sediment sections from the Mudpatch: (A) non-metric multidimensional scaling (nMDS) ordination plots based on Bray Curtis similarity resemblance matrix of OTUs derived from 16S rRNA gene sequencing. 2D stress = 0.05. Labels represent sample depth in cm. Circles show similarity of 40% (green), 60% (blue), and 80% (light blue). (B–F) 2D Bubble nMDS plots of Bray Curtis similarity resemblance showing relative abundance of microbial families. Larger bubble size corresponds to higher relative abundances. (B) *Desulfobulbus*; (C) *Lutimonas*; (D) *Psychrobacter*; (E) *Thaumarchaeota* C3 group; (F) *Planococcus*. The fractional relative abundance of the respective family/genus at each given depth increment is shown in the key. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and nature of this sediment core. The decrease in this zone of the *Desulfobulbaceae* but increase of *Desulfobacteraceae* (Fig. S4), two closely-related families of sulfate-reducers, suggests the core maintains anaerobic conditions at depth. The microbial communities within the 8–28 cm zone was 60% similar, reflected in their clustering on the Bray Curtis nMDS plot (Fig. 3A). Here the presence of putatively aerobic families, such as the *Phyllobacteriaceae* ($1 \pm 0.3\%$) (Willem, 2014) and the anaerobic *Desulfobacteraceae* ($2.1 \pm 0.3\%$) and *Anaerolineaceae* ($4.3 \pm 1\%$) (Fig. S4) appear to show that the dominant redox conditions are heterogeneous, likely comprised of relatively high Eh anaerobic (denitrification, manganese, and iron reduction) processes. The presence of sulfate-reducers implies there is some degree of sulfate-reduction occurring. A lack of methanogenic taxa, such as the *Euryarchaeota*, signals a lack of this function. The microbial community data from the Esk

Estuary suggests there is a transition in community assemblage as a function of depth, but with the maintenance of the complex heterogeneous mix of oxidising and reducing redox functions. The presence of the *Hyphomicrobiaceae* ($0.9 \pm 0.1\%$) (Fig. S4) is also indicative of a low carbon, high Eh environment (Oren and Xu, 2014), and LOI results subsequently showed an average of ~5% total organic matter in the core. This suggests that the labile organic matter reservoir (i.e. excluding the highly refractory component) may be small.

On balance, our results suggest that the Esk Estuary sediment is more microbially active than the Mudpatch, as evidenced by the distinctive microbial distribution patterns observed, but that these patterns are likely dictated by a complex and dynamic hydrological regimen, consistent with tidal influences in this estuarine setting. Here, subsurface and surface inundations of aerobic tidal waters likely give rise to cyclic

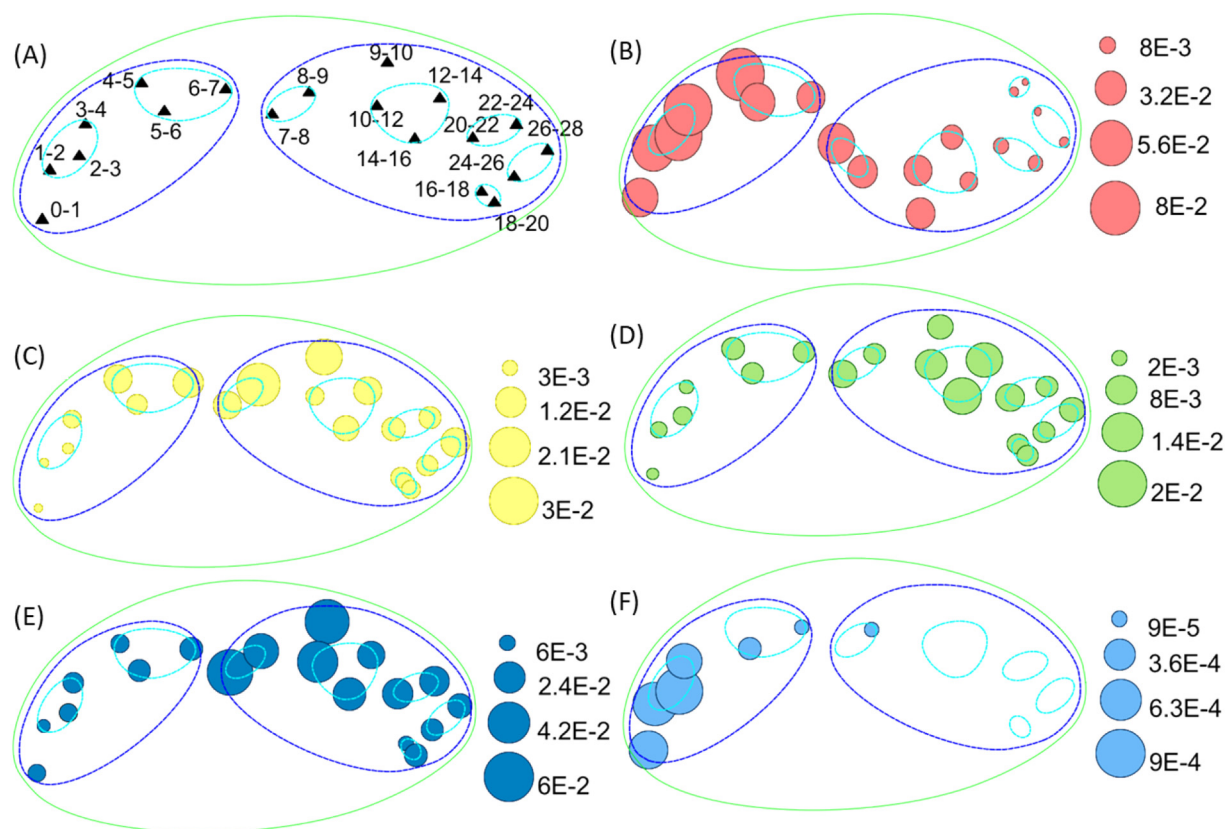


Fig. 3. For sediment sections from the Esk Estuary: (A) Non-metric multidimensional scaling (nMDS) ordination plots based on Bray-Curtis similarity resemblance matrix of OTUs derived from 16S rRNA gene sequencing. 2D stress = 0.02. Labels (top left) represent sample depth in cm. Circles show similarity of 40% (green), 60% (blue), and 80% (light blue). (B–F) 2D Bubble nMDS plots of Bray-Curtis similarity resemblance showing relative abundance of microbial families. Larger bubble size corresponds to higher relative abundances. (B) *Desulfobulbus*; (C) *Thaumarchaeota*; (D) *Bathyarchaeota*; (E) SEEP SRB-1; (F) *Draconibacterium*. The fractional relative abundance of the respective family/genus at each given depth increment is shown in the key. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

transitions from oxidising to reducing conditions in areas of preferential water flow.

3.3. Radionuclide distribution and partitioning in the Irish Sea Mudpatch

The ^{137}Cs activity concentrations in the Mudpatch core ranged between 120 and 220 Bq/kg, with the activity increasing with depth until ~15 cm (albeit with variation) and then remaining >170 Bq/kg to the bottom of the core (Fig. 4A). The activities of ^{238}Pu and $^{239,240}\text{Pu}$ at the Mudpatch also increased with depth, ranging from 26 to 140 Bq/kg, respectively at the sediment surface, to ~55–300 Bq/kg by 15 cm depth (Fig. 4C and D). Thereafter, the ^{238}Pu and $^{239,240}\text{Pu}$ activity concentrations were more constant with depth, except for much higher values (92 and 551 Bq/kg) at 25 cm. Plutonium-241 activity concentrations were also measured at the Mudpatch (Fig. 4E) and whilst the lowest activity concentration was found at the sediment surface (~700 Bq/kg), the ^{241}Pu values in the rest of the core varied between 2000 and 4000 Bq/kg without a discernible trend. The depth distribution of ^{241}Am in the Mudpatch was broadly similar to that of ^{137}Cs , with the ^{241}Am activity concentrations ranging between 193 and 504 Bq/kg (except for a single sample at the bottom of the core where the activity concentration was 750 Bq/kg) (Fig. 4B). Similar ^{137}Cs , Pu, and ^{241}Am activity concentrations and distributions were described for a Mudpatch core taken in 2002 (Gouzy et al., 2005) and have also been reported from a range of Mudpatch surface sediment and core samples taken in the 1980s and 1990s (e.g. Kershaw et al., 1983; Kershaw et al., 1999; McDonald et al., 2001; Jones et al., 2007). ^{241}Pu decay in the Mudpatch

sediments will also contribute to the ^{241}Am activity concentrations at this site, but given that the Mudpatch is heavily bioturbated, it is impossible to accurately account for ^{241}Am at the site.

Select samples from the Mudpatch core underwent sequential extraction in an attempt to understand how the Sellafield-derived radionuclides were partitioned in the sediment and if there were changes with depth. For ^{137}Cs and ^{241}Am , 10 samples underwent extraction and there was little variation in the data down-core (Fig. 5). The majority of the Cs was associated with the 'residual' fraction (~40–60%), whilst ~30–40% was 'exchangeable', 20–30% was 'reducible'; the balance was 'oxidisable'. Cesium preferentially associates with clay minerals in sediments, often substituting for other cations in the clay interlayer (e.g. Fuller et al., 2015). The Mudpatch sediments have a clay fraction of ~13% (McDonald et al., 1990) and a large proportion of the more recalcitrant Cs in the sediment samples is likely bound in clay mineral interlayers. In contrast, the exchangeable and reducible Cs fractions probably reflected weakly sorbed Cs on clay mineral surfaces, organic matter, and/or Fe/Mn oxy(hydr)oxides (e.g. Sawhney, 1972; Ferris et al., 2000). ^{241}Am was not associated with the 'exchangeable' or 'reducible' sediment fractions in any of the Mudpatch sediment samples (again, 10 samples underwent extraction). Instead, a minor fraction of the ^{241}Am was extracted in the 'oxidisable' fraction (1–12%), and the rest was associated with the 'residual' fraction (87–98%). McDonald et al. (2001) have also reported ^{241}Am extraction data from Mudpatch surface sediments, albeit using a different extraction scheme. In their work, the majority (>70%) of the ^{241}Am was found in the more recalcitrant sediment fractions (organics/inorganic

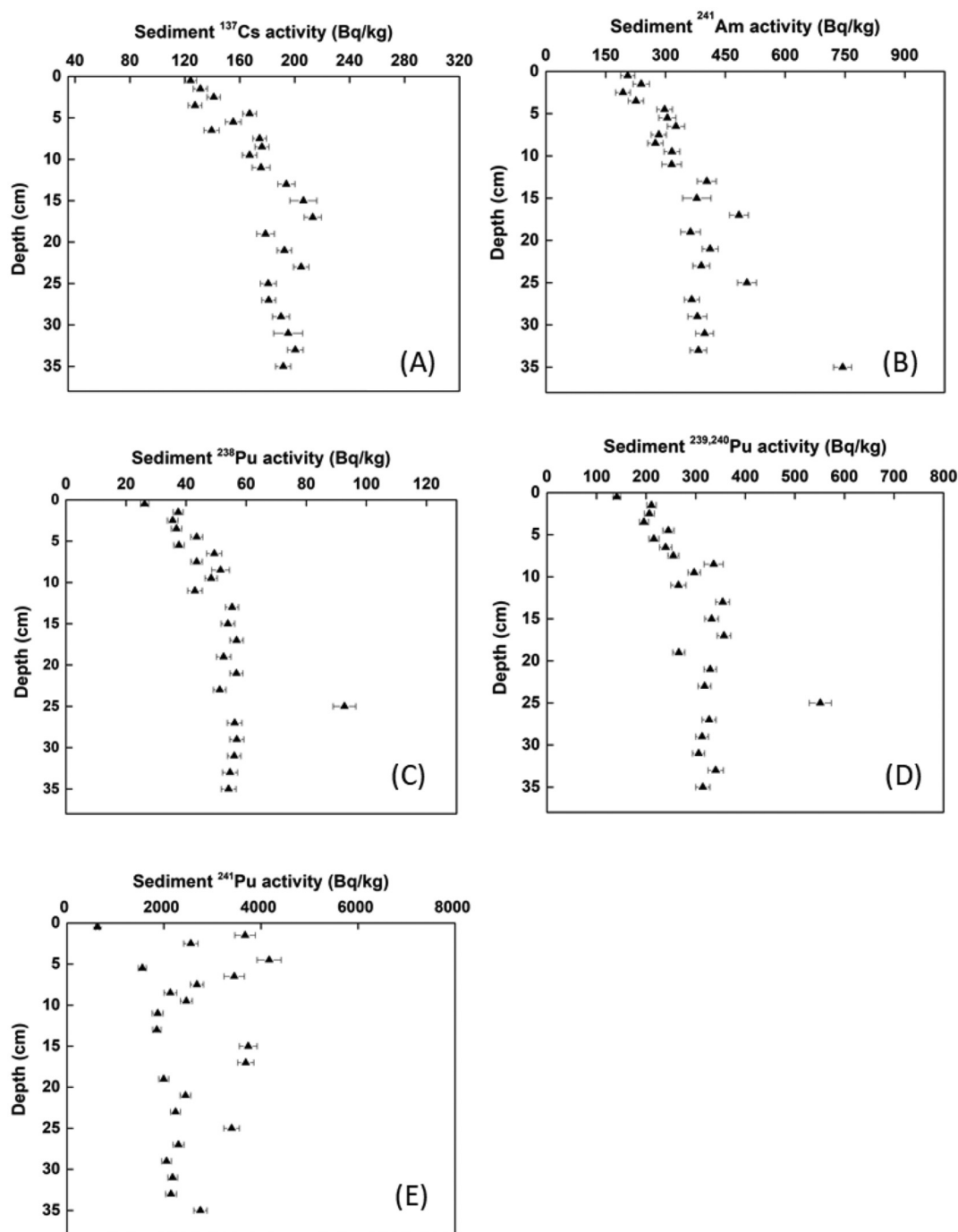


Fig. 4. Activity concentrations of (A) ^{137}Cs , (B) ^{241}Am , (C) ^{238}Pu , (D) $^{239,240}\text{Pu}$, and (E) ^{241}Pu in the Mudpatch sediment core (error bars are 1σ based on counting errors).

oxides), however a larger proportion of their ^{241}Am (~20%) was found in the exchangeable fraction.

Only two samples (3.5 cm and 25 cm) underwent extraction for Pu, and only $^{239,240}\text{Pu}$ was measured in the extraction solutions. In the 3.5 cm sample (run in duplicate), $^{239,240}\text{Pu}$ was mainly found in the reducible (39–48%) and residual fractions (38–56%), with smaller proportions present in the exchangeable (<5%) and oxidisable fractions (<10%). Plutonium partitioned in a similar way in the deeper sample and, in past work at the Mudpatch, McDonald et al. (2001) also found that Pu was mainly associated with reducible-oxides. Laboratory experiments in the last four decades have shown that Pu has a high affinity for Fe and Mn oxy(hydr)oxides (e.g. Sanchez et al., 1985; Keeney-Kennicutt

and Morse, 1985; Morgenstern and Choppin, 2002; Shaughnessy et al., 2003; Fjeld et al., 2003; Powell et al., 2005), and that Pu can be sequestered under microbially-mediated Mn/Fe reducing conditions (Lloyd et al., 2005; Ohnuki et al., 2007). Such associations may account for the sizeable fraction of Pu found in the reducible fraction of both sediment samples, although comparison of the Mudpatch Pu, Fe, and Mn profiles and the microbial ecology data (Figs. 1, 2, and 4) provide no obvious evidence to suggest that there is a biogeochemical control governing contemporary Pu distribution at this site. As such, the link between Fe, Mn, and Pu may represent coincident leaching of other Pu host phases coincident with Fe and Mn. Interestingly, our work and that of McDonald et al. (2001) also contrasts with the work of Gouzy

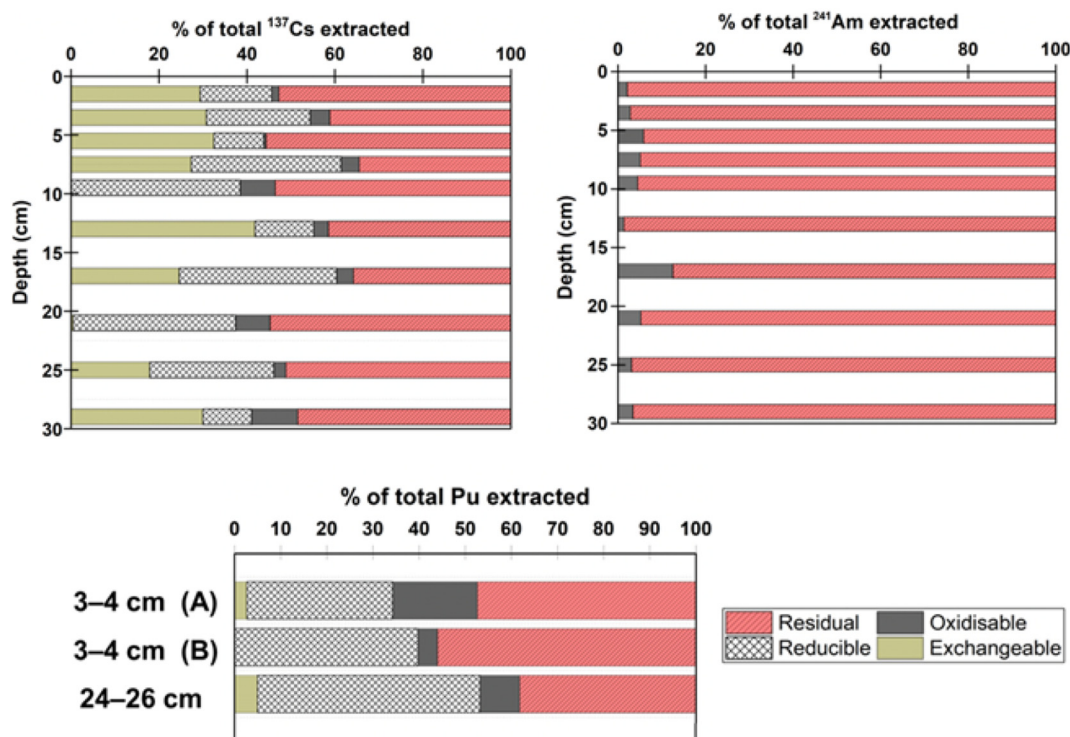


Fig. 5. Percentage of total extractable ^{137}Cs , $^{239,240}\text{Pu}$, and ^{241}Am liberated with each targeted “fraction” of the Mudpatch sediment when using the sequential extraction procedure detailed in Table 1.

et al. (2005) who found that >60% of Pu in their Mudpatch sediment samples was associated with “exchangeable” and “acid soluble” phases (e.g. AVS). This would suggest that Pu may respond more strongly to microbially mediated redox reactions/diagenetic reactions elsewhere on the Mudpatch, and in turn be more “available” (e.g. through oxidative dissolution of AVS phases). Alternatively, differences in the extraction protocols used may account for the contrast in the studies. Gouzy et al. (2005) added 0.175 M of Na-citrate to each of their extraction steps (after Lucey et al., 2004) in an effort to limit possible re-adsorption of dissolved Pu onto the sediment phase. Further work is thus necessary to address these contrasts.

Whilst biogeochemical controls may control part of plutonium's contemporary distribution at the Mudpatch, the combined effects of decreasing radionuclide inputs from the Sellafield site, and physical mixing of the sediments are also likely to also influence its distribution, as well as ^{137}Cs and ^{241}Am . Contemporary Sellafield radioactivity discharges to the Irish Sea are now >1 order of magnitude lower than those from the 1960's–1980's. However, this decrease in Sellafield derived Cs, Am, and Pu supply to the Irish Sea (Sellafield Ltd., 2017) is clearly not reflected in the Mudpatch activity concentration profiles (Fig. 4). Indeed, the surface sediment activity concentrations reported here are broadly similar to those reported in the 1980s. If the Mudpatch sediments recorded the Sellafield discharge history, the contemporary sediment activity concentrations should decrease more sharply towards the sediment surface. Further, the radionuclide activity ratios (Fig. S6) should also reflect trends in the discharge records (Table S4). As this is not observed, physical mixing of higher activity sediments from depth (i.e. those deposited when the discharges were greater) into shallower sediment horizons, must play a role in governing the contemporary radionuclide distributions at this site.

In past work, several authors have shown that Sellafield-derived radionuclides penetrate to >1 m at the Mudpatch, reflecting pervasive bio-mixing. This was also indicated by our microbial ecology data from this site (Fig. 2). Bioturbation and burrow irrigation are known to facilitate

downward mixing of the radionuclides into deeper sediment horizons (e.g. Kershaw et al., 1983; MacKenzie et al., 1998; Cournane et al., 2010). However, those processes also bring older radionuclide-labelled sediments towards the surface. The sediment-associated radionuclides can be remobilised into the water column (e.g. via dissolution or sediment resuspension), and be transported elsewhere (Hunt and Kershaw, 1990). As such, the Irish Sea Mudpatch likely provides a long-term source of contemporary, as well as older Sellafield derived radionuclides to other locations in the Irish Sea (e.g. Hunt and Kershaw, 1990; MacKenzie et al., 1994; Marsden et al., 2006; Al-Qasbi et al., 2016, 2018). Here, given the sequential extraction data (Fig. 5), it is likely that Cs and Pu are lost from the Mudpatch in both aqueous and particle-bound forms, whilst Am is likely lost in particle-bound form.

3.4. Radionuclide distribution and partitioning in the Esk Estuary

3.4.1. Esk Estuary sediment dating

Past authors have shown that the Esk Estuary receives a steady input of sediment and Sellafield derived radionuclides (e.g. Morris et al., 2000; Marsden et al., 2006). Esk Estuary sediments also undergo limited/physical mixing and as a result, the sediment profile appears to record changes in the Sellafield discharge history (Morris et al., 2000). As such, activity peaks in the discharge history can be used to date the Esk Estuary sediment profile relative to peaks in the discharge history (if one assumes a constant sediment rate) (e.g. Morris et al., 2000; Marsden et al., 2006). Therein, any deviation in the radionuclide distribution profile away from that of the discharge trends, may signal post-depositional remobilisation. With that in mind, the ^{137}Cs , ^{241}Am , and Pu depth distributions in our Esk Estuary sediment core are presented in Fig. 6 alongside (i) an additional ‘date’ axis, and (ii) historical Sellafield discharge data for these radionuclides. The method for calculation of the “date” axis was that used in previous work (Marsden et al., 2006). The reader should also note that Morris et al. (2000) and Marsden et al. (2006) observed a ~2 year offset between the Sellafield discharge

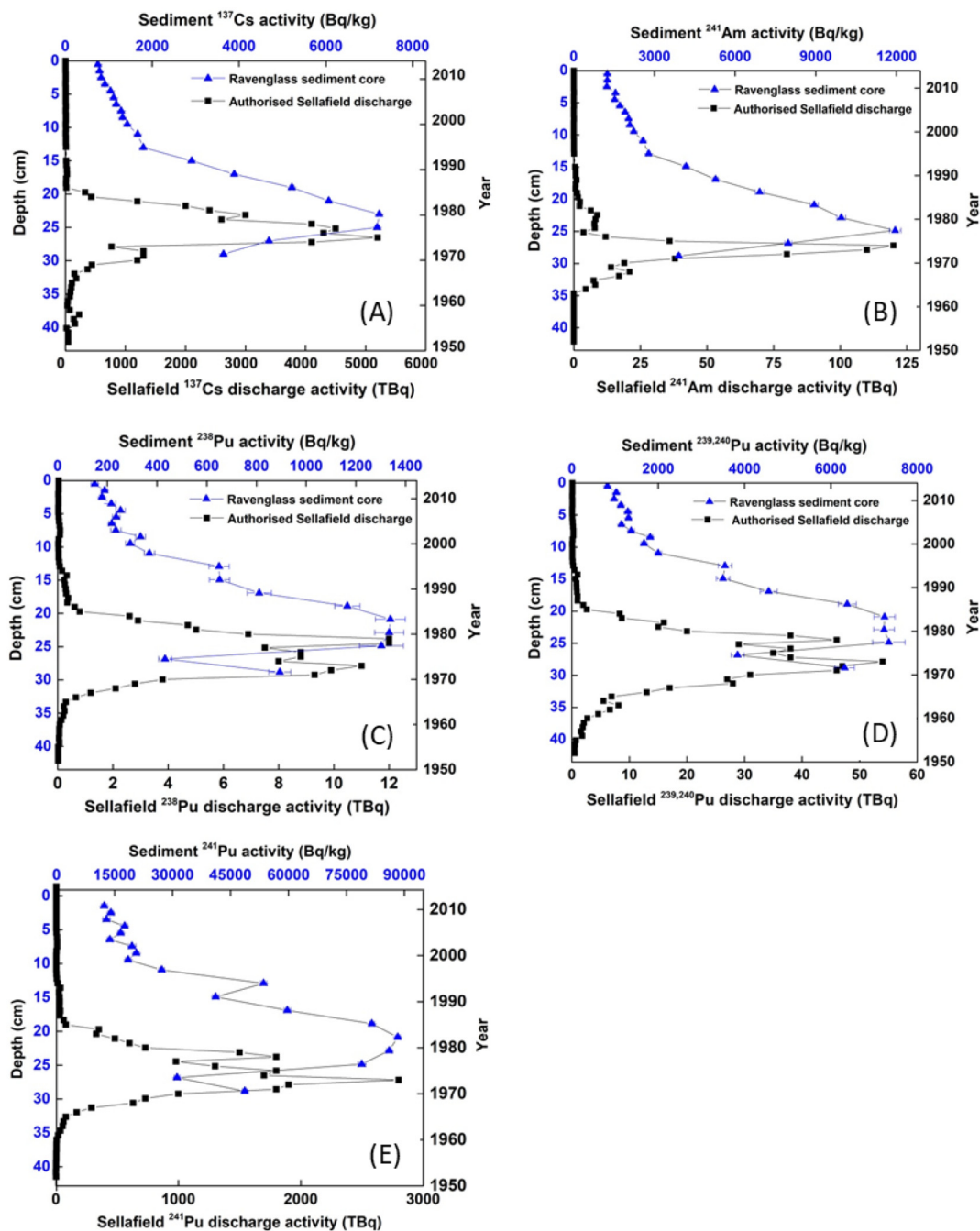


Fig. 6. Activity concentrations of (A) ^{137}Cs , (B) ^{241}Am , (C) ^{238}Pu , (D) $^{239,240}\text{Pu}$, and (E) ^{241}Pu in the Esk Estuary sediment core (black) dated using the Sellafield discharge history (blue) (error bars are 1σ based on counting errors, and may be smaller than markers). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

records and Esk Estuary core profiles, and this was attributed to transport of Sellafield-derived radionuclides from the waste pipeline, and in turn, radio-labelled sediments from the Mudpatch to the Esk Estuary.

3.4.2. Cesium-137

The ^{137}Cs activity concentration in the Esk Estuary core increased steadily (700–1800 Bq/kg) from 0 to 13 cm sediment depth. Thereafter, there was a sharp increase in activity with added depth, reaching a maximum of ~7200 Bq/kg at 23 cm (Fig. 6A). The activity then decreased to 3600 Bq/kg by 30 cm. The ^{137}Cs activity concentrations and depth profile reported here are similar to those presented by Lucey et al. (2004) and Marsden et al. (2006); however, the activity concentrations are

lower than those reported by Morris et al. (2000) (who reported a range of 2000–35,000 Bq/kg), showing possible heterogeneity in ^{137}Cs deposition across the estuary as previously indicated (Horrill, 1984). The Esk Estuary ^{137}Cs activity concentrations reported here (regardless of depth) are also much higher than those found at the Mudpatch (Fig. 4).

Sequential extraction of the Esk Estuary sediments (Fig. 7) showed that the largest proportion of ^{137}Cs was associated with the residual fraction (50–68%), which accounts for a slightly larger proportion (~10–20%) of ^{137}Cs compared to the Mudpatch sediment (Fig. 5). Variable amounts of ^{137}Cs from the Esk sediment were also extracted in the other fractions (exchangeable: 1–22%; reducible: 10–22%;

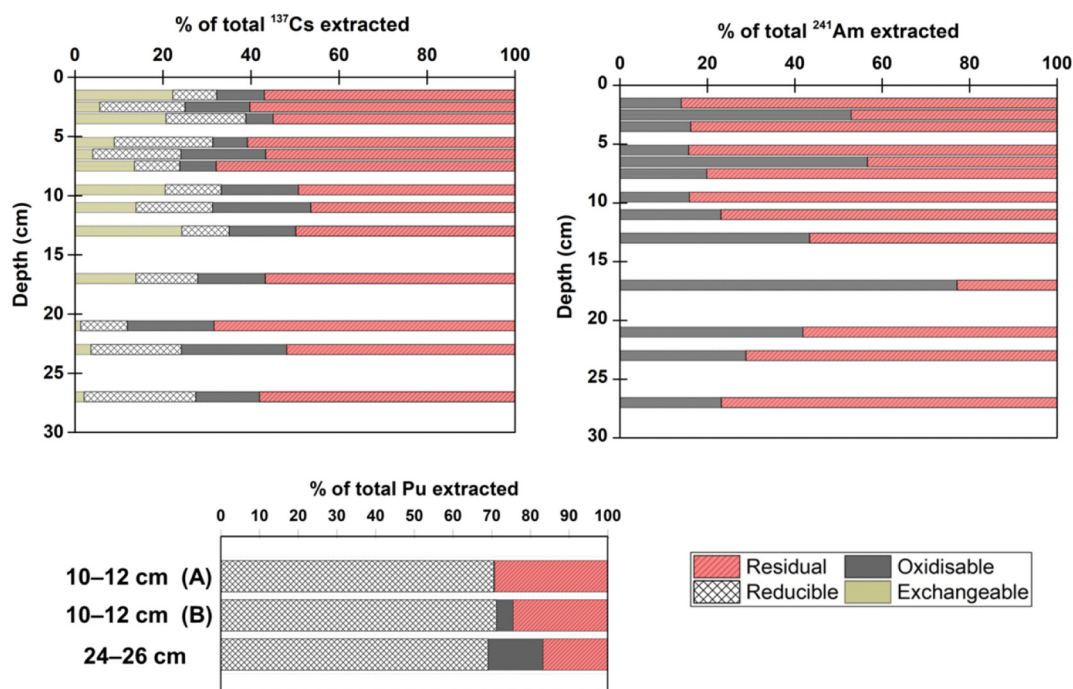


Fig. 7. Percentage of total extractable ^{137}Cs , $^{239,240}\text{Pu}$, and ^{241}Am liberated with each targeted “fraction” of the Ravenglass sediment when using the sequential extraction procedure detailed in Table 1.

oxidisable: 6–22%). Trends in partitioning with depth and ^{137}Cs concentration were largely absent apart from the decreased amount of exchangeable ^{137}Cs found in the deeper (>20 cm) Esk sediment horizons. Interestingly, this trend was not evident at the Mudpatch. Previous work with Esk Estuary sediments has shown that sediment profiles record the Sellafield discharge trend (Kershaw et al., 1990; Livens et al., 1994; MacKenzie et al., 1994; Morris et al., 2000; Marsden et al., 2006) and it is likely that the maximum in the Sellafield ^{137}Cs discharge record (Fig. 6A) manifests as the activity concentration “peak” in the Esk core. The broadening of the peak in the sediment profile compared to the discharge history likely reflects a combined supply of ^{137}Cs in seawater and ^{137}Cs sediment from the Mudpatch, as well as the relatively low K_d for Cs which should afford it a reasonable degree of post-depositional mobility. However, the reduction in exchangeable ^{137}Cs with depth may reflect the gradual ^{137}Cs uptake into clay interlayers. Finally, it is interesting to note the disparity between the Esk Estuary surface ^{137}Cs concentrations and those of the contemporary Sellafield discharge records (Fig. 6A) and the activity concentrations recorded at the Mudpatch (Fig. 4A). The disparity indicates that cesium input to the contemporary Esk Estuary either includes a source of higher activity ^{137}Cs labelled materials than that can be supplied from the Mudpatch, or that there is a greater degree of post-depositional ^{137}Cs mobility with the Esk Estuary sediment profile than is accounted for in sequential extractions.

3.4.3. Plutonium

The Esk Estuary ^{238}Pu and $^{239,240}\text{Pu}$ activity concentrations (Fig. 6C and D) increased steadily in the top 11 cm of the sediment profile, ranging between 140 and 400 Bq/kg (^{238}Pu) and 800–2000 Bq/kg ($^{239,240}\text{Pu}$). Thereafter, a sharp increase in activity was observed with depth, reaching a maximum of ~1300 Bq/kg at 21 cm (^{238}Pu), and ~7300 Bq/kg at 25 cm ($^{239,240}\text{Pu}$). The final two sections of the core showed variable Pu activity concentrations. The maximum $^{239,240}\text{Pu}$ activity concentrations reported here are comparable to those reported by Lucey et al. (2004) and Lindahl et al. (2011), but are half those reported by Morris et al. (2000) and Marsden et al. (2006). ^{241}Pu activity concentrations were also measured for the Esk Estuary sediments and these ranged between 12 and 88 kBq/kg, with the

sediment depth profile broadly comparable to the other Pu isotopes (maximum activity found at 23 cm; Fig. 6F). Marsden et al. (2006) observed a ^{241}Pu activity concentration between 1 and 242 kBq/kg, and the surface spatial distribution measured by Oh et al. (2009) was also similar to that reported here.

The discharge histories for ^{238}Pu and $^{239,240}\text{Pu}$ (Fig. 6C and D) show two distinct peaks during the 1970s (Gray et al., 1995). In our Esk sediment profiles, there is a broad single peak for ^{238}Pu and $^{239,240}\text{Pu}$; this may reflect a time-averaged deposition of Pu-labelled sediments from the Mudpatch, as discussed by other authors (e.g. MacKenzie et al., 1994; Morris et al., 2000; Marsden et al., 2006). The resolution of the sediment core described here may also prevent fine details from the Sellafield record being observed, as each section represents ~2–3 years of effluent discharge. However, of note, all of the Pu activity concentrations reported for the Esk Estuary, including the surface sediments, are ~1 order of magnitude higher than those reported from the Mudpatch sediments (Fig. 4C–E). This may indicate that Pu supplied to the Esk Estuary has arrived from multiple sources, that some areas on the Mudpatch must support much higher Pu concentrations, or that the Pu deposited in the Esk sediments has some degree of post-depositional remobilisation.

Similar to the Mudpatch, two samples from the Esk Estuary (10–12 cm and 24–26 cm) underwent sequential extraction to investigate Pu partitioning in the sediment, and only $^{239,240}\text{Pu}$ was measured in the extracts. For the 10–12 cm sample, the majority of the Pu was extracted in the reducible fraction (71–75%). In turn, 24–31% of the Pu was extracted with the residual fraction, with the balance associated with the oxidisable fraction (0–4%) (Fig. 7). Plutonium partitioning was similar for the 24–26 cm sample, although slightly more Pu was associated with the oxidisable (14%) fraction. This data is comparable to the Pu partitioning described for the Mudpatch sediments, and again suggests that a sizable proportion of the Pu in the Esk Estuary samples may be associated with reducible Fe/Mn oxy(hydr)oxides. However, as with the Mudpatch, comparison of the Pu distribution with sediment Fe, Mn, and microbial ecology data reveals no obvious biogeochemical control. In past Esk Estuary work, Mudge et al. (1988) and Kimber et al. (2015) also found that the majority of the Pu in the sediment was associated with the residual and reducible fractions during

sequential extractions. In contrast, Lucey et al. (2004) found that the >50% of Pu in Esk sediment was either exchangeable or associated with more reactive sediment fractions (e.g. carbonates, easily oxidisable sulfides). As per the work of Gouzy et al. (2005), Lucey et al. (2004) added high concentrations of Na-citrate (0.175 M) into their extractions to stop possible re-adsorption of extracted Pu onto the sediment. In turn, they interpret their data as an indication of significant Pu reaction with sulfides and carbonates in the Esk sediment profile. Again, further work is needed to resolve Pu mobility in the Esk Estuary.

3.4.4. Americium-241

The ^{241}Am activity concentrations in the Esk Estuary core increased steadily for the first 13 cm of the sediment profile, rising from ~1.2 to ~2.8 kBq/kg (Fig. 6B). Thereafter, a sharp increase in activity was observed with increased depth, reaching a maximum of ~12 kBq/kg at 25 cm (Fig. 6B). The ^{241}Am activity concentration then decreased steadily to ~4 kBq/kg by 30 cm. These activity concentrations are comparable to those presented by Lucey et al. (2004) and Marsden et al. (2006), and again they are significantly higher than the activity concentrations (~190–500 Bq/kg) reported from the Mudpatch (Fig. 4). Sequential extraction of the Esk Estuary sediments showed that ^{241}Am was almost exclusively partitioned between the residual (22–85%) and oxidisable (14–77%) sediment fractions, and there was no discernible trend with depth and/or ^{241}Am activity concentrations (Fig. 7). The amount of ^{241}Am associated with the oxidisable fraction was also much higher in the Esk Estuary sediments compared to the Mudpatch (1–12% of extracted ^{241}Am).

Interestingly, the ^{241}Am Esk sediment profile has a broader peak compared to the Sellafield ^{241}Am discharge record. Indeed, the ^{241}Am distribution in the Esk sediment core is similar to that described for ^{137}Cs . This is at first surprising given that Am is particle-reactive and poorly soluble in seawater, and that ^{241}Am supply to the Esk Estuary has been suggested to (primarily) reflect the input of ^{241}Am labelled sediments from the Mudpatch (Morris et al., 2000; Marsden et al., 2006). However, as shown in the SI (Fig. S5), the decay of Sellafield derived ^{241}Pu in the Esk Estuary sediment likely controls a large proportion of the extraneous ^{241}Am distribution, and as such Am is likely to be quite immobile in the Esk Estuary sediment.

3.5. ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios

The ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios can provide information on the source of Pu. The ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios for samples in the Mudpatch core were between 0.15 and 0.21 (Fig. S6A). This suggests that the origin of Pu is not from weapons material (as this would have an activity ratio of <0.03) and instead originates from Sellafield discharges derived from civil fuel reprocessing. The ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios for the Esk core range between 0.11 and 0.20 (Fig. S6B) and this was slightly lower than ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios observed in the Sellafield discharge history which have been ~0.33 since 1979 (Table S4; note that after 1992 discharged Pu has been recorded as total- α , thus the ratio of 0.33 is assumed). This ratio highlights that the source of Pu deposited at the Esk Estuary arises from civil nuclear operations, with no indication of the presence of lower burn-up material. In addition, lower ratios (0.1–0.14) observed at the bottom of the Esk core may reflect some Pu remobilisation in older, deeper sections (~26–30 cm) of the core. The examination of a deeper core at the site would be required to determine whether ^{238}Pu : $^{239,240}\text{Pu}$ activity ratios continue to decline.

4. Conclusions and implications

Cesium-, Pu-, and ^{241}Am -containing low-level aqueous effluent is legally discharged from the Sellafield site into the Eastern Irish Sea. Prior to improvements in effluent treatment at the Sellafield site (1980s), discharged activities were much higher. At the point of discharge, Pu,

^{241}Am , and some ^{137}Cs associates with offshore fine-grained sediments at the Irish Sea Mudpatch. Based on the geochemistry and microbial ecology of the sediment, Pu distribution at this site appears to be largely independent of redox controls; instead Pu (and ^{137}Cs and ^{241}Am) distribution is controlled by sediment mixing at the site. This in turn re-suspends radiolabelled sediments, which are then transported elsewhere in the Irish Sea. The nearby Esk Estuary has received and still appears to receive a supply of radiolabelled sediment from the Mudpatch and/or elsewhere in Irish Sea, despite an ever-decreasing discharge of radioactivity from the Sellafield site. Again, Pu distribution at the Esk Estuary appears to be largely independent of redox controls. Instead, its distribution appears to be largely controlled by physical processes (sedimentation at the Mudpatch followed by later bio-mixing, re-suspension, sediment transport, and eventual re-deposition). Plutonium was also shown to be associated with two strongly bound phases, reducible oxides and the residual phase. This trend was reflected at both the Mudpatch and Esk Estuary, and suggests Pu is unlikely to be bioavailable/mobile, however, the limitations of sequential extractions need to be considered.

The majority of the Am and Cs inventory at both sites was present in the strongly bound residual fraction, with Cs also being extracted in the easily accessible exchangeable fraction, which reflects its higher mobility. The same processes appear to control ^{137}Cs and ^{241}Am distribution at Esk and after sedimentation there appears to be some (^{137}Cs) to limited (^{241}Am) radionuclide remobilisation, and instead the radionuclide activity depth profiles record the time-integrated Sellafield discharge records. These findings for the Esk Estuary are similar to those of past workers (Lucey et al., 2004; Marsden et al., 2006; Lindahl et al., 2011) and as such, the ^{137}Cs , ^{241}Am , and Pu activity maxima should be further buried with time. However, a key observation from this work is the presence of ^{137}Cs , ^{241}Am , and Pu in the surface sediments of the Irish Sea Mudpatch, in contrast to the low contemporary activity release from the Sellafield site. This suggests that bioturbation at this site will continue to act as a source of “historic” Sellafield-derived radioactivity to the UK Coastal Environment.

CRediT authorship contribution statement

Daisy Ray: Investigation, Writing - original draft. **Peter Leary:** Investigation, Writing - original draft. **Francis Livens:** Funding acquisition, Investigation, Writing - original draft. **Neil Gray:** Funding acquisition, Investigation, Writing - original draft. **Katherine Morris:** Investigation, Writing - review & editing. **Kathleen A. Law:** Investigation, Writing - review & editing. **Adam J. Fuller:** Investigation, Writing - review & editing. **Liam Abrahamsen-Mills:** Investigation, Writing - review & editing. **John Howe:** Investigation, Writing - review & editing. **Kieran Tierney:** Investigation, Writing - review & editing. **Graham Muir:** Investigation, Writing - review & editing. **Gareth T.W. Law:** Funding acquisition, Investigation, Writing - original draft.

Declaration of competing interest

The authors declare no competing interests. The data and views reported in this paper do not represent those of the UK Government Department for Business, Energy, and Industrial Strategy.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.140765>.

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